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RADIATIVE LIFETIME AND COLLISIONAL QUENCHING KINETICS FOR THE X--ETC(U)
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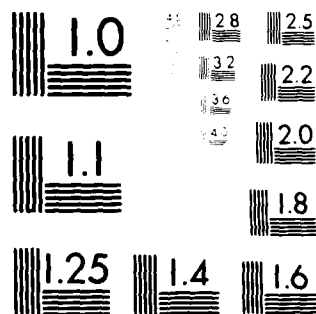
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RADIATIVE LIFETIME AND COLLISIONAL QUENCHING
KINETICS FOR THE XeF (B 1/2) STATE*

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ABSTRACT

A state-selective laser-induced-fluorescence technique has been used to determine the radiative lifetime and collisional quenching kinetics for the XeF (B 1/2) excited state. Ground state XeF molecules, formed by flash dissociating a mixture of UF_6 and Xe diluted in He, are excited to the B state by a 3511 Å XeF laser pulse. The subsequent fluorescence decay of the $v' = 0$ level is monitored at 3533 Å using a spectrometer-fast photomultiplier combination. Collisional quenching rate coefficients for the collision partners He, Ne, Xe, F_2 , and NF_3 are reported. Broadband fluorescence emission at 460 nm has also been observed and is interpreted to result from collisional transfer from the B to the C state of XeF.

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I. INTRODUCTION

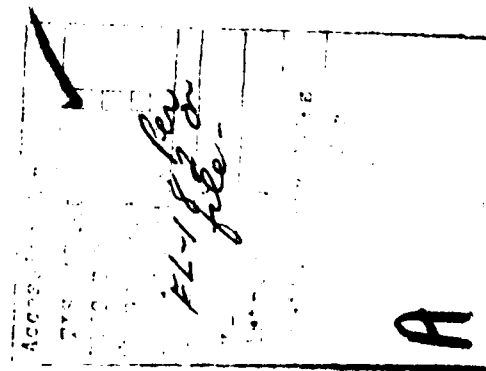
There has recently been intense interest in the rare gas halide lasers because they have been shown to have the potential for high efficiency, scalability to large volumes and high power levels, and transmission through the atmosphere. The optimization of lasing performance and the scaling to large systems requires a kinetic model of the rare gas halogen system which incorporates the relevant mechanisms for the excitation and destruction of the upper and lower laser levels. There has been considerable experimental and theoretical investigation of the possible kinetic mechanisms leading to the formation of the electronically excited upper state. However, until recently, very little information on the radiative lifetime of the upper state or the rate constants for collisional destruction processes had emerged.

The radiative lifetime of the XeF(B)^1 state has recently been measured utilizing electron beam dissociative excitation of $\text{XeF}_2^{2,3}$ and ArF laser photodissociation of $\text{XeF}_2^{4,5}$. Collisional deactivation rate coefficients for some of the species of interest in laser gas mixes have been determined from a Stern-Volmer analysis of the $\text{XeF (B} \rightarrow \text{X)}$ emission resulting from the steady state photolysis of XeF_2^{6} . Bimolecular and termolecular quenching rate coefficients for some of the rare gases have been determined using a steady state analysis of the $\text{XeF (B} \rightarrow \text{X)}$ emission produced by electron beam excitation of Ar/Xe/ F_2 or Ne/Xe/ F_2 gas mixtures.⁷ More recently, the radiative lifetime and

collisional deactivation of the XeF (B) state has been determined using photolysis of XeF₂ with pulsed ArCl emission (175 nm).⁸ All of these techniques have the disadvantage that the excitation processes are not state specific, and therefore a distribution of vibrational and electronic excited states is produced. The results obtained from these experiments represent, therefore, an average over the particular excited state distribution produced. This may vary depending upon the specific excitation technique employed.

We have employed a laser-excited fluorescence decay technique to determine the radiative lifetime and collisional deactivation rate coefficients for the XeF (B) state. The optical excitation technique is state specific and permits the measurements to be made in an environment free of other interfering excited states and charged particles. A small concentration of F atoms is produced by flash photolysis of a mixture of UF₆ and Xe diluted in He. After a time delay to allow the Xe and F atoms to form an equilibrium concentration of XeF, some of the ground state molecules are excited to the B electronic state by a short duration XeF laser pulse. The subsequent temporal decay of the B state is followed by monitoring the B → X fluorescence.

In addition to the 353-nm fluorescence, we have observed broad-band emission at 460 nm, which we interpret to be the C → A transition. From the temporal behavior and pressure dependence of the 460-nm emission, it is inferred that the C state is formed by collisional transfer from the B state.



II. EXPERIMENT

A schematic diagram of the experimental arrangement is shown in Fig. 1. Fluorine atoms are first prepared by flash dissociating a mixture of F_2 or UF_6 plus Xe and a monatomic diluent (usually He). In our initial experiments, we were able to obtain fluorescence emission from XeF (B) using a mixture of F_2 and Xe diluted in He. Both XeF_2 and UF_6 were also tried as F atom sources. The XeF_2 yielded a very weak fluorescence signal, presumably because of the poor overlap between the XeF_2 absorption spectrum and the flashlamp emission spectrum. However, the intensity of the emission increased an order of magnitude when UF_6 was substituted for F_2 as the F atom donor. This is due to the fact that UF_6 has a larger absorption cross-section in the near ultraviolet than F_2 .⁹ The increased signal allowed a much wider range of gas mixtures to be explored.

When UF_6 is used as the fluorine atom source, particles of UF_5 precipitate after the mixture is flashed. These particles cause strong scattering of the exciting laser on subsequent shots. As a result, each gas fill can only be used for one shot. To verify that the observed signal was not due to laser light scattered from these particles, a gas mixture containing only He and UF_6 was photolyzed under the same conditions as the mixes containing Xe. No fluorescence emission was obtained for delays of tens of milliseconds after the first flash when Xe was omitted from the gas mixture.

The photolysis cell is constructed from quartz tubing arranged in a cross configuration with ultraviolet grade fused silica windows sealed to the end of each tube. The cell is mounted inside a double ellipsoidal aluminum reflector with the long arm of the cross located on the common axis of the two ellipses. Two linear flashlamps (ILC 4D3) are located on the other axes of the ellipses, one above and one below the plane of the cross. The exciting laser beam traverses the cell parallel to the flashlamps, while the fluorescence is viewed perpendicular to the exciting beam through a window on the cell. The cell is evacuated by an oil diffusion pump equipped with an anti-creep, liquid nitrogen cooled baffle. Gas samples are introduced to the cell through a high purity stainless steel manifold which was passivated with F_2 before use.

Gas mixtures for the experiment were premixed on a separate diffusion pumped manifold and then transferred to the photolysis cell apparatus in stainless steel bottles. The mixing manifold and the sample cylinders were thoroughly passivated before use by exposure to F_2 . Pressures below 14 torr were measured with a variable reluctance pressure transducer (Validyne AP10) and pressures above 14 torr were measured with 0-760 torr Bourdon gauges. The fluorescence cell was pumped down to 10^{-6} torr and then filled with new gas before each shot in order to eliminate any impurities created by F atom reactions at the walls.

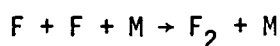
The He, Ne, and Ar (Linde high purity grade), and the Xe (Matheson research grade) were used directly from the bottle without further purification. The NF_3 was purchased from Rocketdyne and was degassed by

cooling to 77 °K and pumping on it. The F_2 was purchased from Matheson and was distilled from a cylinder cooled to 77 °K in order to trap HF. The UF_6 was obtained from Allied Chemical Company. It was first degassed at 77 °K and then warmed to 195 °K and pumped on again to remove HF.

After a delay of about one millisecond to allow the Xe and F atoms to form an equilibrium concentration of ground state XeF, the resulting molecules were excited to the XeF* (B) state with a XeF laser pulse at 3511 Å ($B \rightarrow X, v' = 0 \rightarrow v'' = 2$ and $v' = 1 \rightarrow v'' = 4$).¹⁰ The minimum delay is determined by the time for the equilibrium concentration of XeF to form while the maximum delay is set by the time for F atoms to recombine to form F_2 . Appelman and Clyne¹¹ report a rate constant of $2 \times 10^{33} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ for the reaction



while the rate constant for the F atom recombination



is $8 \times 10^{-35} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ for $M = Ar$ ¹² and $6 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ for $M = He$.¹³ For 10 torr Xe, 250 torr Ar, and 0.1 torr F, the minimum time would be 200 μsec and the maximum delay (for He) would be about 60 msec. We have observed fluorescence signals with delays ranging from 100 μsec to 10 msec, although most of the data was obtained with delays from 0.5 to 2 msec.

The XeF laser used in these experiments was a Blumlein-excited electric discharge device equipped with ultraviolet preionization.¹⁴ The laser was forced to operate at 3511 \AA by using a 1800 groove/mm diffraction grating as one of the cavity elements. The opposite end of the optical cavity is formed by a 10-cm plano-convex lens placed with the convex side facing the active medium. This unstable cavity configuration, reported recently by Barker and Loree,¹⁵ significantly reduces the beam divergence, thus reducing laser light scattered from the cell walls. Using a gas mixture of He + 1 percent Xe + 0.5 percent F_2 at 2-atm total pressure, the laser output energy is about 10 to 15 mJ with a pulse duration of 10 nsec (FWHM). The laser pulse decays with a time constant of 4 to 5 nsec, which sets an upper limit on the measured fluorescence decay rate.

The intensity of the $v' = 1 \rightarrow 4$ band relative to the $v' = 0 \rightarrow 2$ band for typical XeF lasers is approximately 0.5 to 1.^{16,17} If the absorption cross-sections for the two transitions are the same (this is consistent with the Franck-Condon factors calculated by Smith and Koblinsky¹⁰), then the number of molecules excited to the $v' = 0$ and $v' = 1$ level of the B state will be determined by the population of the $v'' = 2$ and $v'' = 4$ levels of the ground state. Assuming that the ground state vibrational levels are in thermal equilibrium and using the spectroscopic constants of Smith and Koblinsky,¹⁰ the number of molecules excited to the $v' = 1$ level of the B state is estimated to be 20 percent of the number excited to $v' = 0$. Further evidence that the $v' = 0$ level of the B state is predominantly excited was obtained by searching for fluorescence

from the $v' = 1$ level at 347 and 345 nm. Only very weak emission was observed indicating that the $v' = 1$ population is much less than that of $v' = 0$.

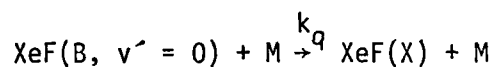
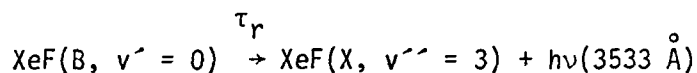
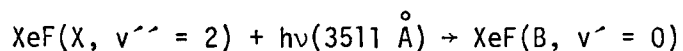
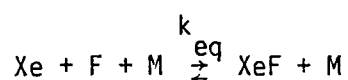
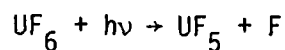
The exciting laser pulse was monitored using a vacuum photodiode (ITT F 4000-S1) and a 3511 \AA interference filter. The subsequent decay of the XeF (B) state was then followed by observing the fluorescence emission at 3533 \AA (XeF B \rightarrow X, $v' = 0 \rightarrow v'' = 3$) using a 0.25 meter spectrometer and a fast photomultiplier (RCA 1P28). The bandwidth of the spectrometer equipped with a 2360-groove/mm grating and 0.5-mm slits is 10 \AA .

In order to improve the time response of the photomultiplier, the phenolic base was removed from the 1P28 and the pins were soldered directly to a low inductance tube base constructed from printed circuit board.¹⁸ The 3-nsec time response of the photomultiplier was verified by comparing its response to scattered 3511 \AA laser radiation with that of the vacuum photodiode, which has a rise and fall time of less than 1 nsec. The photodiode and photomultiplier responses were displayed on a Tektronix 7844 oscilloscope (400 MHz bandwidth) and photographed on Polaroid film. The decay curves were read directly from the oscilloscope traces. For most of the gas mixtures studied, the 3533 \AA emission could be fit by a single exponential decay once the exciting laser pulse terminated. The decay rates were obtained from least square fits to decay data covering two or more e-folding periods.

III. RESULTS

A. 353-nm Emission

The sequence of reactions describing the formation and decay of the XeF (B) state in our laser excited fluorescence experiment is as follows:



The differential equation describing the production and loss of the B state can be written

$$\begin{aligned} \frac{d}{dt} [\text{XeF}(\text{B})] = & I(t)\sigma[\text{XeF}] - [\text{XeF}(\text{B})](\tau_B^{-1} + k_{\text{He}}[\text{He}] + k_{\text{Xe}}[\text{Xe}] \\ & + k_{\text{UF}_6}[\text{UF}_6]) \end{aligned}$$

where the brackets denote concentration, σ is the XeF absorption cross-section, $I(t)$ is the intensity of the exciting laser pulse, τ_B is the radiative lifetime of the XeF (B) state, and k_i is the quenching rate constant for the i^{th} component of the mixture. Once the pump laser pulse

has terminated, the XeF (B) state will decay exponentially with a time constant given by

$$\tau^{-1} = \tau_B^{-1} + k_{\text{He}} [\text{He}] + k_{\text{Xe}} [\text{Xe}] + k_{\text{UF}_6} [\text{UF}_6]$$

The XeF (B) radiative lifetime is obtained by determining the decay time constant as a function of pressure for a gas mixture with fixed composition. A plot of the reciprocal of the decay time constant versus pressure should yield a straight line with a zero pressure intercept that is the radiative lifetime.

Such a plot for one series of experiments is shown in Fig. 2. The straight line indicates the least squares fit to the data. The intercept taken from this fit along with the statistical uncertainty is indicated in the figure. Two other experiments using different gas mixtures yielded lifetimes of 17.3 ± 2.3 nsec and 22.4 ± 2.0 nsec. An average of these three radiative lifetimes using the respective statistical uncertainties as weighting factors yields a value of 19.4 ± 1.0 nsec for the XeF (B) state radiative lifetime. This value is compared with those obtained by other workers in Table I. The most recent lifetimes obtained from the dissociative excitation of XeF₂ are somewhat shorter than the value obtained in the present work. One possible difference between the two techniques arises from the fact that in the other experiments cited, emission from the various vibrational levels of the B state was not spectrally resolved. Dissociative excitation of XeF₂ produces several vibrational levels of the XeF (B) state which may have lifetimes different

than that of the $v' = 0$ level. Thus, the lifetimes reported in those experiments represent averages over the vibrational distribution produced in the XeF_2 photolysis. In the present work, predominantly the lowest XeF (B) vibrational level is produced and monitored.

Collisional quenching rate coefficients for various species are obtained by measuring the XeF (B) decay time constant as a function of the partial pressure of that constituent. If bimolecular quenching is dominant, the slope of the straight line fit to the data gives the quenching rate coefficient. We have determined collisional quenching rate coefficients for He, Ne, Xe, F_2 , and NF_3 in this manner. Plots of the data for F_2 and Xe along with the straight lines that were least squares fit to the data are shown in Figs. 3 and 4. The numbers obtained for the other species in the same way are listed in Table II.

No data are shown for collisional deactivation by Ar. This is due to the fact that the 353-nm fluorescence in the presence of Ar exhibited non-exponential decay over much of the pressure range studied. However, it is possible to obtain a qualitative estimate of the quenching rate coefficient due to Ar from the intercepts determined for the straight line fits to the Xe quenching data (Fig. 4). Two separate sets of experiments were conducted, one with Ar as the diluent and one with He as the diluent. These data suggest that the Ar quenching rate coefficient is comparable to that of He.

The XeF (B) collisional quenching rate coefficients determined in the present experiment are summarized in Table II and compared with those obtained by other workers. The uncertainties listed in the table are the statistical uncertainties obtained from the least squares fitting procedure. The value listed for Ne is the statistical uncertainty since it was larger than the actual slope determined, and therefore represents an upper limit to the rate coefficient. The low quenching rate coefficient for Ne suggests that from a collisional deactivation standpoint, Ne is preferable to Ar or He as a diluent for XeF laser gas mixtures. This may partly explain the improved extraction efficiency obtained in electron-beam excited and electron-beam-sustained-discharge excited XeF lasers using Ne instead of Ar as a diluent.¹⁹

The measured rate coefficients also indicate that, if only collisional deactivation is considered, NF₃ should be preferable to F₂ as the fluorine atom source.

From Table II, it is evident that the agreement between the rate coefficients determined in the present experiments and those reported by other workers using dissociative excitation of XeF₂ is satisfactory for the case of Xe but much poorer for the other species. Again, one source of disagreement between the various experiments may be the different vibrational distribution for the XeF (B) state produced by the different excitation techniques.

Our values for the XeF (B) quenching rate coefficients by NF₃ and F₂ are considerably lower than those determined by the other workers.

For NF_3 , we have a few preliminary data points taken at lower pressures than those used to obtain the rate constant listed in Table II, which suggest that the NF_3 quenching rate coefficient may be a factor of two higher than the value reported in the table. However, the data points do not cover a wide enough pressure range to be conclusive.

One explanation for the low quenching rate coefficient for F_2 could be loss of F_2 by wall reactions. To verify that this was not a problem, several experiments were carried out varying the time between filling the cell and firing the flashlamps. No difference in decay rate was observed for times from less than a minute to as long as 10 minutes, indicating that loss of F_2 was not important.

An attempt was also made to investigate termolecular collisional quenching effects by using He, Ne, and Ar pressures as high as three atm. However, at pressures above 1 atm, the 353-nm emission exhibited non-exponential decay, suggesting either collisional coupling with some other excited state which can act as a reservoir or excited state-excited state self-destruction. Excited state self-destruction can be dismissed since the XeF (B) number density is so low in these experiments ($\leq 10^{10} \text{ cm}^{-3}$). The most likely candidate for this collisional coupling is the XeF (C) state, which according to the theoretical calculations of Dunning and Hay,²⁰ should be nearly degenerate with the B state.

B. 460-nm Emission

According to the theoretical calculations of Dunning and Hay,²⁰ the XeF (C) state potential curve lies very close to the B state. They

calculate that the allowed $C \rightarrow A$ transition will be located at 420 nm, with a lifetime of approximately 100 nsec. This transition is expected to have a 50-nm bandwidth because the A state potential curve is repulsive.

Because of the possibility of collisional transfer from the B state to the C state of XeF, broadband emission centered at approximately 460 nm was looked for and observed. The 460-nm emission was observed in the presence of He, Ne, or Ar as the diluent and with total pressures as low as 150 torr. The amplitude of the emission increased and the time to reach peak decreased when the diluent pressure was increased and when the Xe partial pressure was raised from 10 to 20 torr. This behavior suggests that the state responsible for the 460 nm fluorescence is formed collisionally and not directly by the exciting laser pulse.

Emission at 460 nm has been previously observed by other workers,²¹⁻²³ and is thought to be due to the transition from the bound C state to the repulsive A state of XeF. There was some early speculation that this emission might be due to ArXeF or Xe₂F triatomic molecules.²³ However, we have observed the emission in He/Xe/F₂ and Ne/Xe/F₂ mixtures as well as Ar/Xe/F₂ mixtures. In addition, the emission in our experiments peaks too rapidly (approximately 20 nsec) to be due to Xe₂F* or ArXeF*. Assuming that the rate constant reported by Rokni, Jacob, Mangano, and Brochu of $3 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1}$ for the reaction $\text{XeF}^* + \text{Xe} + \text{M} \rightarrow \text{products}$ ⁷ leads exclusively to XeF* formation, the time constant for 10 torr Xe and 250 torr Ar is 1 μsec . For the same conditions, the rate constant value of $1.5 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$ reported in Ref. 7 for the reaction $\text{XeF}^* +$

$2\text{Ar} \rightarrow \text{products}$ would also have a time constant of 1 μsec . We conclude that the 460-nm emission is due to diatomic XeF, probably the $C \rightarrow A$ transition.

A comparison of the time history of the 353-nm and 460-nm fluorescence obtained at a total pressure of 1.5 atm is shown in Fig. 5. The 460-nm emission displays significantly longer rise and decay times than the 353-nm fluorescence. The longer rise time of the 460-nm emission suggests that the state is populated by collisional transfer from the B state. Evidence for collisional coupling is also available from the behavior of the 353-nm emission. The nonexponential decay of the 353-nm fluorescence in the presence of Ar was mentioned previously. Nonexponential decay is also observed when the He or Ne pressure is increased above 1 atm and is visible in Fig. 5. This behavior is consistent with collisional coupling between the B and C states, which may prove to be an important kinetic process in XeF lasers.

Collisional coupling between the B and the C states modifies the simple exponential decay expected if only bimolecular quenching is considered. The problem of coupled decay has been previously described by several workers, e.g., by Stephenson and Moore²⁴ in connection with laser excited vibrational energy transfer in CO_2 mixtures. In the limit of no mixing, each state has a simple exponential decay with its own characteristic rate, λ_B or λ_C . As collisional mixing becomes important, the B state decays as the sum of two exponentials, $a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t)$, and the C state decays like the difference between two exponentials, $a_3[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]$. Therefore, the C state signal will start at

zero, rise to a maximum, and then decay back to zero, as in Fig. 5. The decay constants, λ_1 and λ_2 are functions of the individual decay constants of the B and C states, λ_B and λ_C , as well as the rate constants for collisional mixing between the states. In the limit of very rapid mixing, both states decay with the same time constant, which is a linear combination of their individual lifetimes.

The 353-nm data was fit to a single exponential decay, ignoring the effects of collisional coupling described above. However, even in the Ar experiments which displayed clear non-exponential decay, the contribution of the slower decaying signal was found to be less than 20 percent.

It should be possible to extract the radiative lifetime and collisional quenching rate coefficients for the XeF (C) state by studying the temporal behavior of the 460-nm emission as a function of gas concentration. By simultaneously studying the 460-nm fluorescence and the 353-nm fluorescence, it should also be possible to determine the rate coefficients for collisional mixing between the B and C states. This work is presently in progress.

ACKNOWLEDGEMENT

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Table I
Summary of Experimental Values of
XeF (B) Radiative Lifetime

AUTHOR	τ_B (nsec)
present work	19.4 \pm 1.0
Eden and Searles ²	16.0 \pm 5.0
Ewing ³	13.5 \pm 1.0
Burnham and Harris ⁴	18.8 \pm 1.3
Burnham and Searles ⁵	15.0 \pm 0.8
Eden and Waynant ⁸	14.25 \pm 0.2

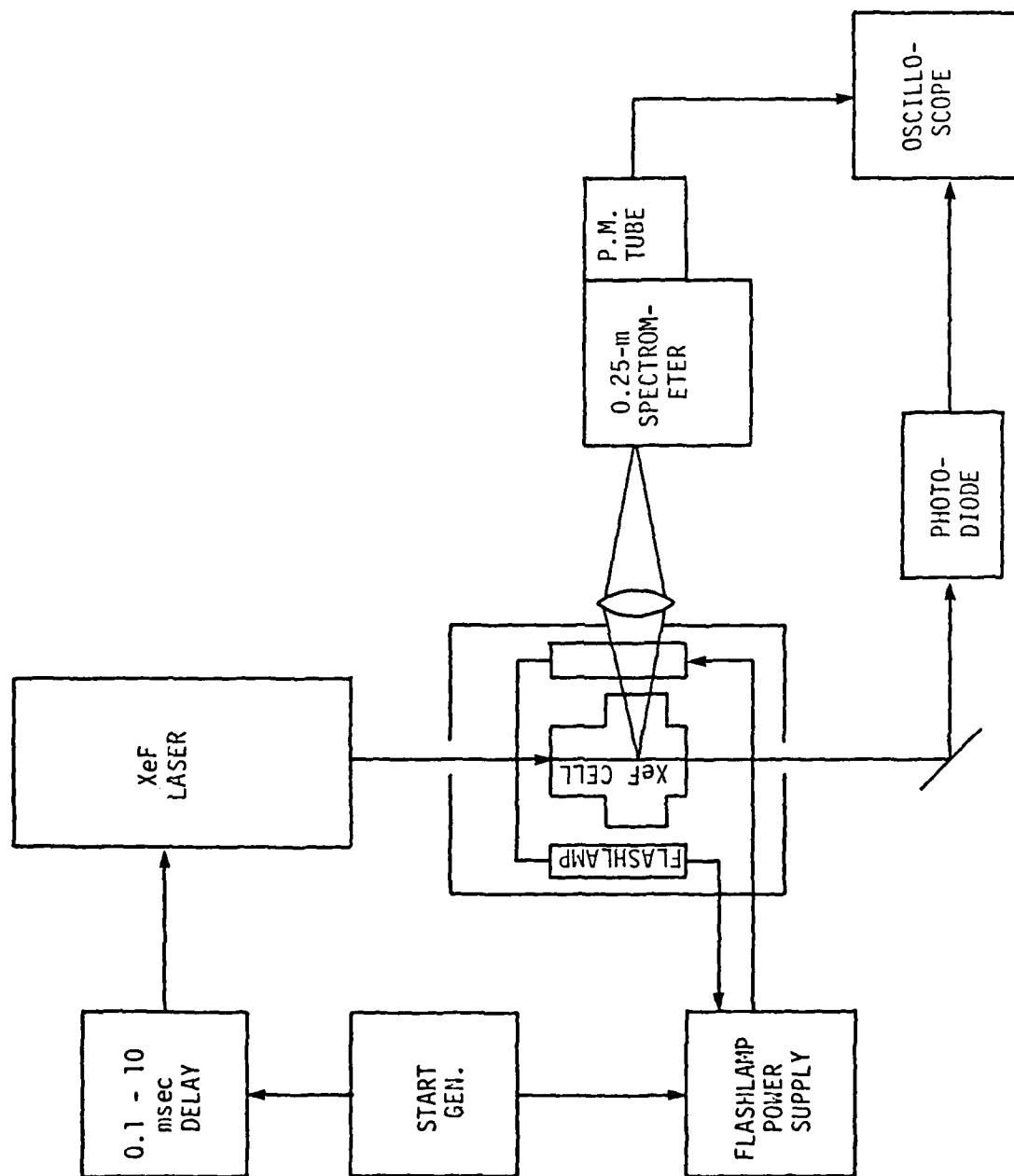
Table II
Quenching Rate Coefficients for the XeF (B) State
($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)

QUENCHER	PRESENT WORK	BRASHEARS, SETSER, & DESMARTEAU*6	EDEN & WAYNANT ⁸	ROKNI, JACOB, MANGANO, & BROCHU ⁷	BURNHAM, HARRIS ⁷
He	$2.0(\pm 0.26) \times 10^{-12}$		$4.1(\pm 1.5) \times 10^{-13}$		
He	$< 3 \times 10^{-13}$		$7.7(\pm 1.6) \times 10^{-13}$		
Ar		$2.4(\pm 0.6) \times 10^{-12}$	$4.9(\pm 1.6) \times 10^{-12}$	$3(\pm 4) \times 10^{-13}$	
Xe	$6.0(\pm 0.25) \times 10^{-11}$	$4.3(\pm 0.8) \times 10^{-11}$	$3.3(\pm 0.7) \times 10^{-11}$		
F ₂	$1.2(\pm 0.1) \times 10^{-10}$	$5.1(\pm 0.3) \times 10^{-10}$	$3.8(\pm 0.13) \times 10^{-10}$		
HF ₃	$3.3(\pm 0.3) \times 10^{-12}$	$2.3(\pm 0.2) \times 10^{-11}$	$2.8(\pm 0.15) \times 10^{-11}$		3.5×10^{-10}
XeF ₂			$2.6(\pm 0.3) \times 10^{-10}$		
CO ₂		$2.5(\pm 0.2) \times 10^{-10}$			
N ₂		$7.0(\pm 1.0) \times 10^{-12}$			

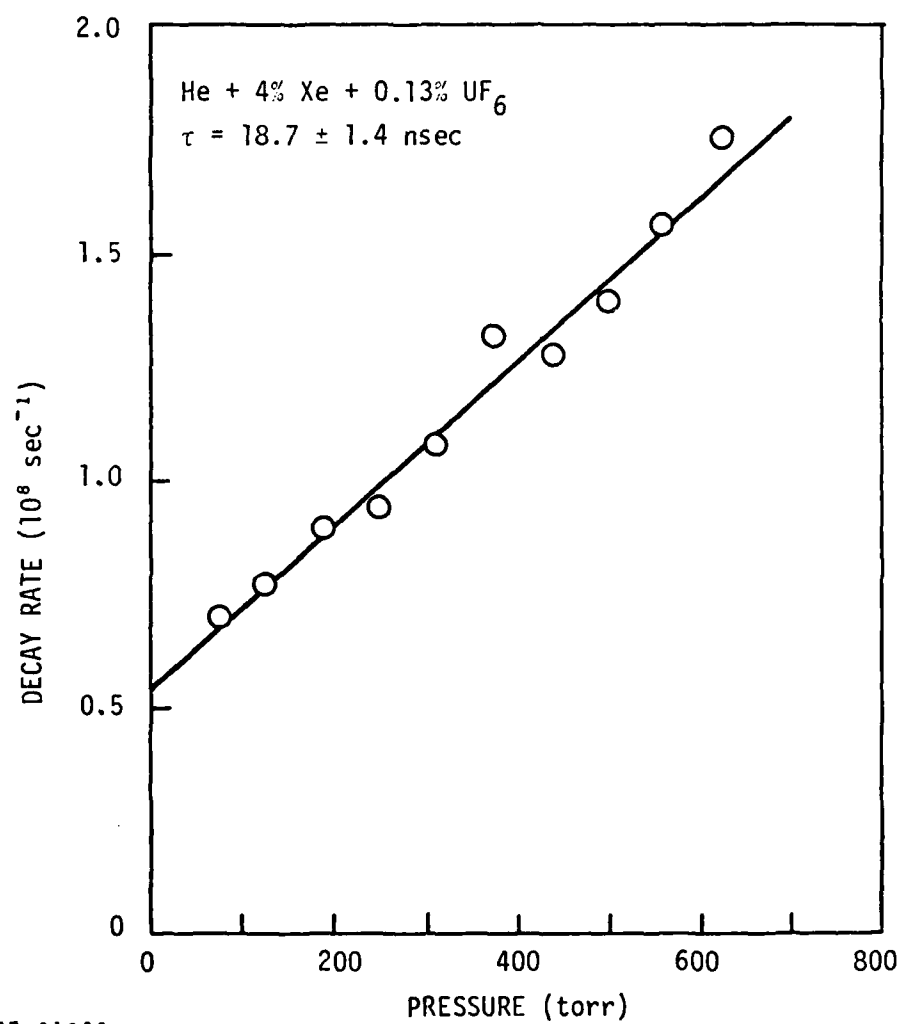
* These rate constants were calculated from the $k\tau$ values reported in Ref. 6 using an effective XeF* lifetime of 10.4 nsec. The value of 16 nsec used in Ref. 6 does not include quenching by the 4 torr of XeF₂ used in the photolysis experiments.

FIGURE CAPTIONS

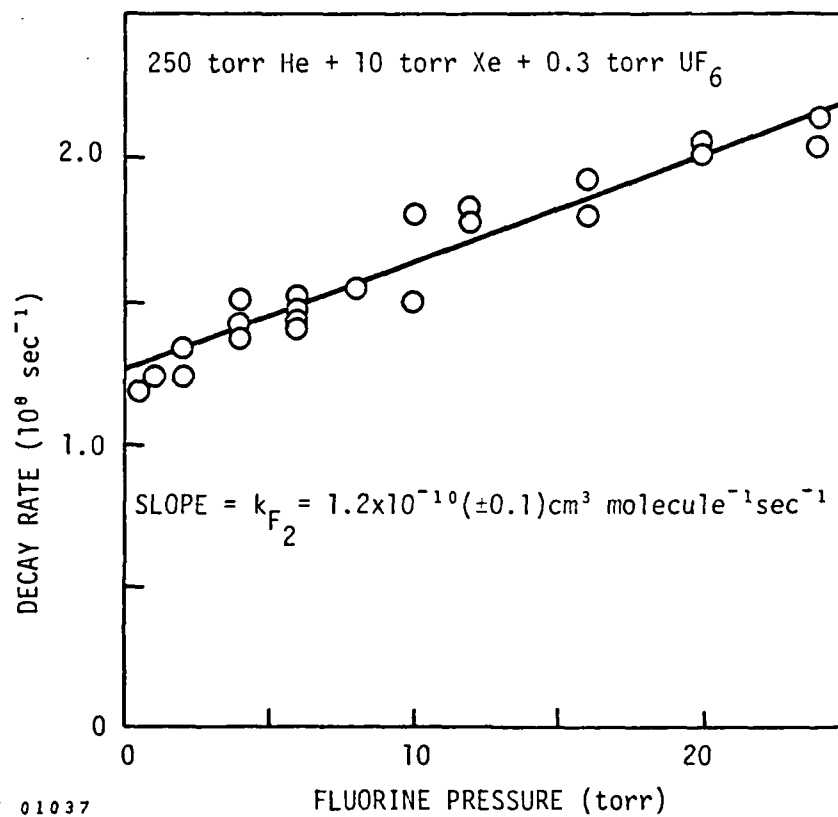
- Fig. 1. Schematic diagram of the laser induced fluorescence experiment.
- Fig. 2. Decay rate as a function of pressure for a He + 4% Xe + 0.13% UF_6 gas mixture. The zero pressure intercept of the straight line fit to the data gives a XeF (B) radiative lifetime of 18.7 (± 1.4) nsec.
- Fig. 3. Variation of the 353-nm fluorescence decay rate as a function of fluorine partial pressure. The slope of the straight line fit to the data gives a quenching rate constant of $1.2 \times 10^{-13}(\pm 0.1)$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.
- Fig. 4. Variation of the 353-nm fluorescence decay rate as a function of Xe partial pressure. One set of experiments utilized Ar as the diluent while the other utilized He. The rate constants determined from the least squares fits to the data are indicated in the figure.
- Fig. 5. Comparison of the time history of the 353-nm and 460-nm emission for a gas mixture of 1.5 atm He + 10 torr Xe + 0.7 torr UF_6 . The intensities of the 353-nm and 460-nm emission have been adjusted so that they have the same peak values.



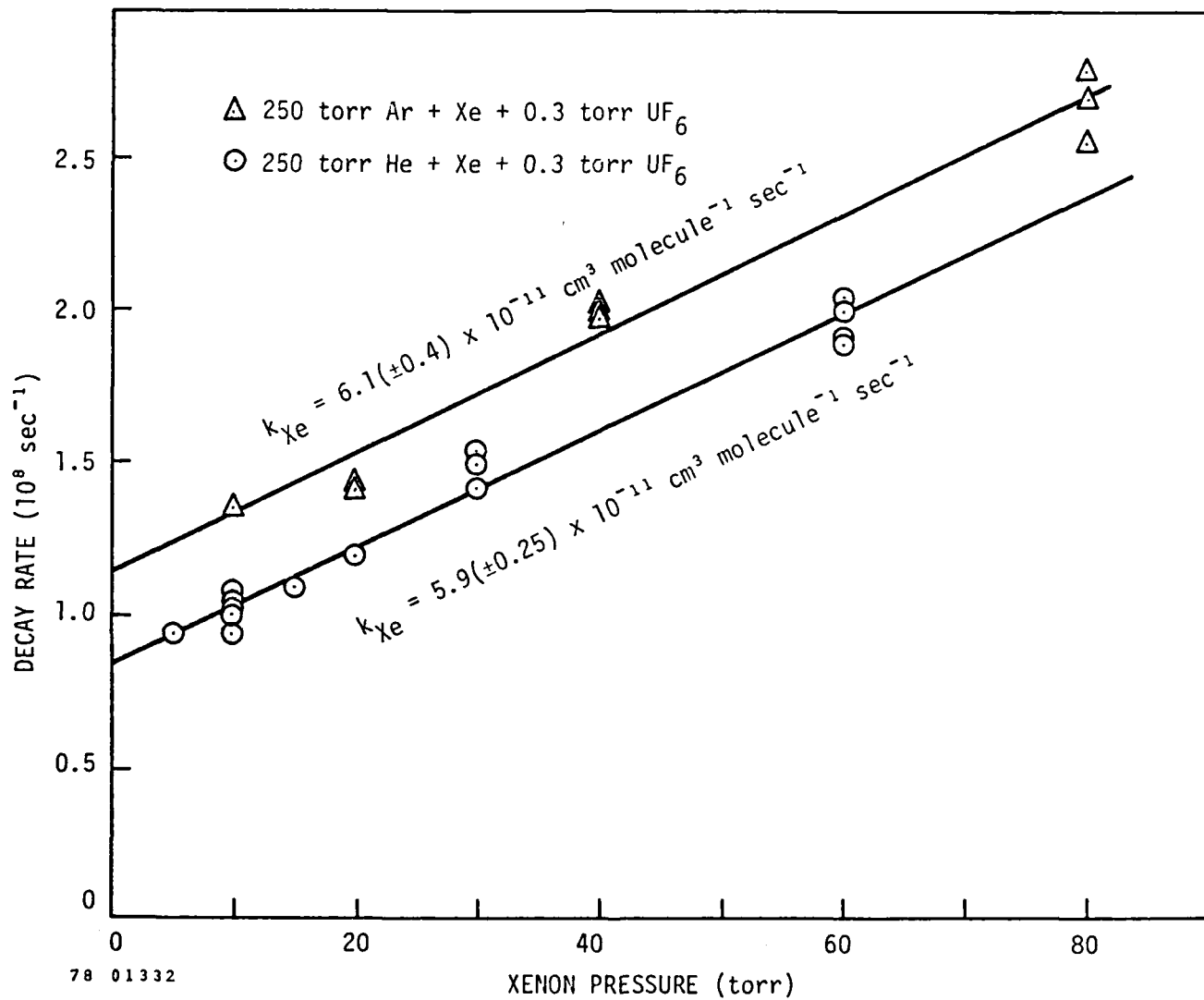
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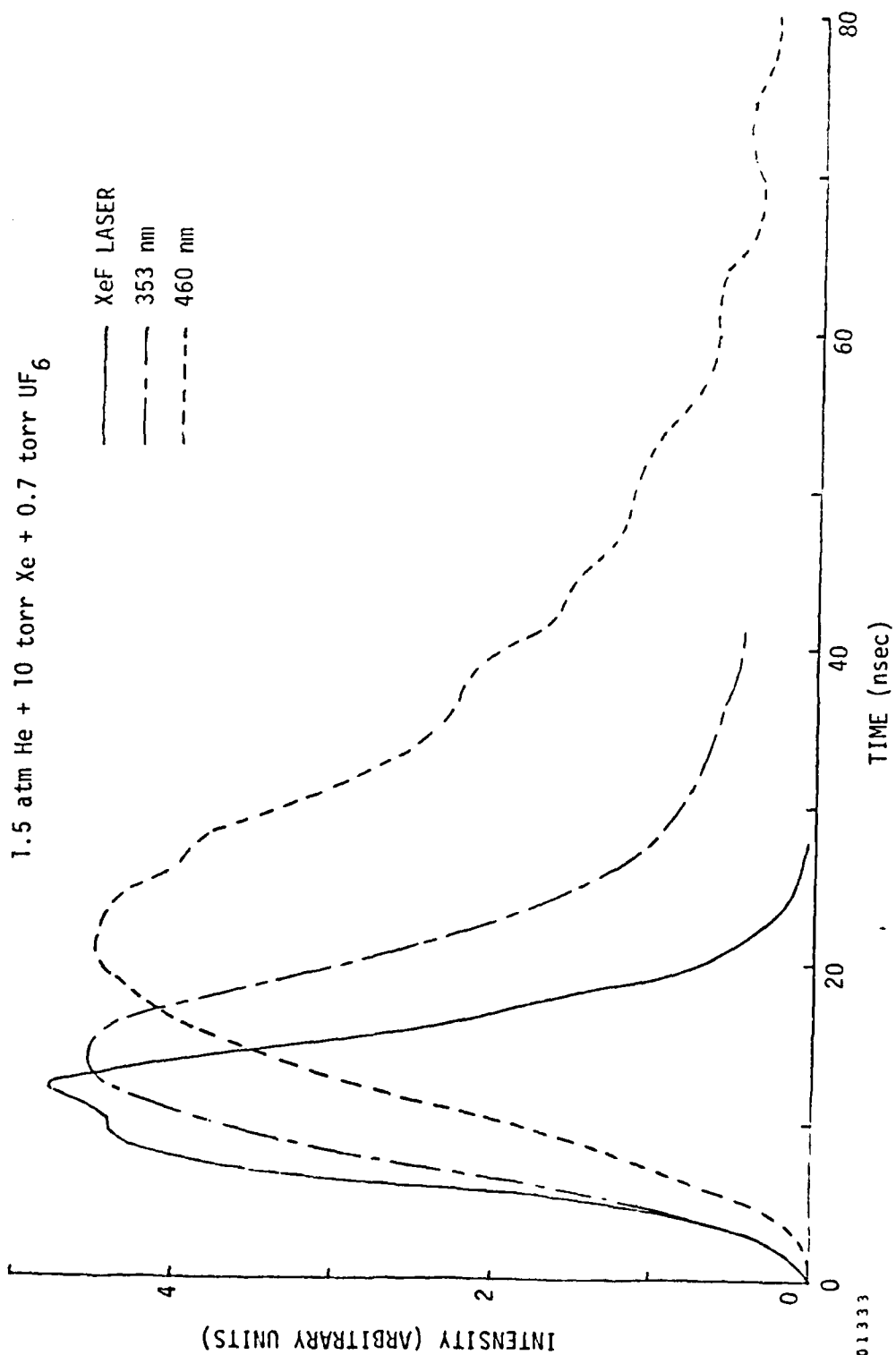


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